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Remarkable Mechanochromism in Blends of a π-Conjugated Polymer P3TEOT: The Role of Conformational Transitions and Aggregation

*Johanna Zessin, Max Schnepf, Ulrich Oertel, Tetyana Beryozkina, Tobias A. F. König, Andreas Fery, Michael Mertig, and Anton Kiriy**

A novel mechanism for well-pronounced mechanochromism in blends of a π-conjugated polymer based on reversible conformational transitions of a chromophore rather than caused by its aggregation state, is exemplified. Particularly, a strong stretching-induced bathochromic shift of the light absorption, or hypsochromic shift of the emission, is found in blends of the water-soluble poly(3-tri(ethylene glycol)) (P3TEOT) embedded into the matrix of thermoplastic polyvinyl alcohol. This counterintuitive phenomenon is explained in terms of the concentration dependency of the P3TEOT's aggregation state, which in turn results in different molecular conformations and optical properties. A molecular flexibility, provided by low glass transition temperature of P3TEOT, and the fact that P3TEOT adopts an intermediate, moderately planar conformation in the solid state, are responsible for the unusual complex mechanochromic behavior.

In the field of material science, one major problem of structural polymers is failure through mechanical stress or strain. Mechanochromic polymers, macromolecules, or their composites, which respond to mechanical stress with a change of their absorption and fluorescence features,[1–3] have been previously considered to monitor the material's failure. A clear color-shift, which requires a shift in the absorption band, would provide a fast, visible warning sign for mechanical stress or deformations in the material. Moreover, mechanochromic polymers might be useful in many emerging materials and applications, e.g., in artificial skin, wearable, camouflage systems, and attoreactor sensors, and for anti-counterfeiting.[4–9]

There are two major approaches to build up polymer-based mechanochromic materials. The first is the incorporation of so-called aggregachromic dyes into polymer matrixes to form thermodynamically stable micro-/nano-sized aggregates.[6,10] Aggregachromic dyes are planar, rigid π-conjugated small molecules, which form J- or H-aggregates through the π-stacking interactions and exhibit distinct optical properties as compared to the monomeric species (bathochromically or hypsochromically shifted absorptions/emissions). The second approach involves a covalent linking of chromogenic units to polymer chains.[11,12] The colorimetric transition can originate from changing molecular interactions, e.g., aggregation,[6,13] or caused by chemical transformations.[11,14,15] Common chromogenic units are organic molecules[16] or organometallic complexes.[17,18] The use of π-conjugated polymers (CPs) as chromogenic units is rare and mainly based on the cis-trans isomerization of acetylene derivatives.[19–22] One of the most abundant mechanisms responsible for the mechanochromism is the aggregation-induced change of the material optical properties (absorption and/or fluorescence) on the response of the mechanical stress.[10,23,24] For such systems to perform properly, the active chromophore should be evenly distributed in the matrix and be present at substantial amounts, around a critical aggregation concentration (typically in 0.1–1% range), which is not always convenient and cheap.

We propose CPs as interesting alternative to aggregachromic dyes for mechanochromic materials. Due to their extended π-conjugated systems along their polymer backbone, CPs possess a strong absorption and luminescence in the visible range of the electromagnetic spectrum. Moreover, their optical properties are very sensitive to any conformational perturbations, as was successfully demonstrated in sensory devices.[25,26] Conformation-induced mechanochromism was already demonstrated

Dr. J. Zessin, M. Schnepf, Dr. U. Oertel, Dr. T. A. F. König, Prof. A. Fery, A. Kiriy
Leibniz Institute of Polymer Research Dresden
Hohe Straße 6, 01069 Dresden, Germany
E-mail: kiriy@ipfdd.de

Dr. J. Zessin, Dr. T. A. F. König, Prof. A. Fery, M. Mertig, A. Kiriy
Cluster of Excellence Center for Advancing Electronics Dresden (cfaed)
Technische Universität Dresden
01062 Dresden, Germany

Dr. J. Zessin, Prof. M. Mertig
Institute of Physical Chemistry
Technische Universität Dresden
01062 Dresden, Germany

Dr. T. Beryozkina
TOSLab
Ural Federal University named after the first President of Russia B.N.Yeltsin
Mira str., 28, 620002 Yekaterinburg, Russia

Prof. M. Mertig
Kurt-Schwabe Institut für Mess- und Sensortechnik e.V. Meinsberg
Kurt-Schwabe-Straße 4, 04736 Waldheim, Germany

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for natural polymers—fluorescent proteins. However, their application as mechanosensors is restricted to biological or at least water-born materials.[27,28] Surprisingly, the mechanochromism in synthetic CPs remains almost unexplored. Recently, Sprakel et al. reported a conjugated polyelectrolyte mechanosensor, which changed its conformation and fluorescence spectra upon an electrostatic complexation with an oppositely charged recombinant coat protein.[29] In literature, mechanochromism is commonly considered as a change of a material's color as response to mechanical forces having a *macroscopic* character and not as a response to added molecules. Accordingly, rather than a mechanochromism, the approach followed by Sprakel et al. can be regarded as a kind of affinitychromism, such as reconformations of charged polythiophenes upon complexation with oppositely charged polymers.[30,31] Poly(3-alkylthiophenes), which are one of the most comprehensively investigated CPs, changes their optical properties only to a minor extend upon the mechanical strain.[20] Their modest mechanochromism can be explained by a relatively planar conformation, which polythiophene molecules adopt in the solid state and polymer blends. Therefore, they are restricted to planarize further upon external stimuli. In solution, on the contrary, polythiophenes can adopt different conformations, which enables a number of "chromisms" phenomena (solvato-, thermo-, affinity-, iono-).[32–34] The chromic transformations in such polythiophenes are driven by a delicate balance between repulsive intra- and inter-chain steric interactions of side groups, and attractive inter-chain π-stacking interactions. The light absorption is determined by individual π-conjugated segments, called effective conjugation length, which can be viewed as quasi-localized chromophores.[35] In good solvents, polythiophene molecules form swollen coils having relatively short conjugation length and, hence, blue-shifted absorption spectra.[35] This state with monomer units isolated from each other by intra-chain twist is equivalent to molecularly dissolved molecular dyes. In solvents poor for the backbone, polymer chains undergo aggregation. Frequently, aggregation is accompanied by the planarization of π-conjugated backbones because planar chains pack more efficiently than twisted ones. The planarization of polymer chains increases the coupling between the covalently bound repeat units within the chain, which can be considered as a case of conventional J-aggregation of head-to-tail-oriented dye molecules. As in the case of the J-aggregation of small molecule dyes, planarization of polymers results in the red-shift of the absorption and fluorescence spectra relatively to those for molecularly dissolved dyes or twisted chains.[35]

Manipulations of microstructure, crystallinity, and molecular orientation of neat CPs, or their blends with structural polymers, such as polyethylenes,[36] polydimethylsiloxane,[37] or polyvinyl alcohol (PVA),[38] were achieved by means of friction-transfer, drawing, stretching, or rubbing. By these procedures, the molecules efficiently align. The resulting films showed an increased charge-carrier mobility in the stretching direction and anisotropic optical properties. Although these stress-induced transformations can be regarded as mechanochromic, the spectral changes were rarely accompanied by an obvious change of the color but can be only monitored in polarized light. Hence, we state, to the best of our knowledge, that practically useful mechanochromism in CPs, was not demonstrated in the literature.

Herein, we report a large mechanochromism occurring upon tensile stretching of the π-conjugated, water-soluble poly(3-tri(ethylene glycol) thiophene), (P3TEOT) blended into the thermoplastic polymer PVA. The chemical structures of both polymers are displayed in **Figure 1**. P3TEOT is structurally related to the milestone polymer P3HT.[39–41] In contrast to P3HT, P3TEOT is well soluble in nonpolar and highly polar solvents including water due to its tri(ethylene glycol) (TEO) side chains. Thus, the polymer is compatible to be blended into a large variety of structural polymers. Unlike previous reports on stretched CPs, P3TEOT/PVA blends show an apparent change of their color upon the stretching from orange to red due to a red-shifted absorption from $\lambda_{max} \approx 460$ to $\lambda_{max} \approx 510$ nm. Polarized absorption spectroscopy indicates that the stretching of the PVA matrix leads to alignment of the polythiophene chains along the drawing direction. To get a deeper understanding of the optical effects and conformational rearrangements of the P3TEOT chains in the PVA matrix, light absorption and fluorescence studies were undertaken for blends in a wide range of P3TEOT concentrations.

P3TEOT, used in this work, was synthesized by the controlled ex situ initiated Kumada catalyst-transfer polycondensation (KCTP) according to modified literature procedures.[39–41] The ex situ initiator was used to obtain a defect-free regioregular polymer. The thiol group is not expected to influence the optical properties of the polymer and was used as it was available. ^{1}H NMR spectroscopy (Figure S1a, Supporting Information) revealed the presence of the ex situ initiator. We used the

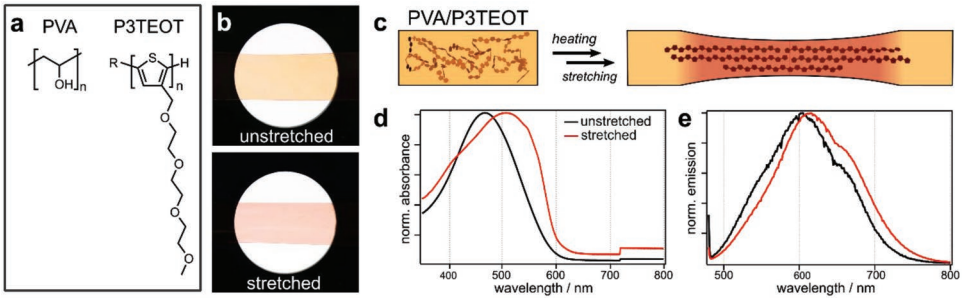

Figure 1. a) Chemical structure of P3TEOT and PVA. b) Photos of the unstretched and stretched polymer blends. c) Schematics of the uniaxial stretching of a PVA/P3TEOT blend. d) UV/vis absorption and e) emission spectra of the unstretched (black lines) and stretched (red lines) blend. Excitation wavelength is 470 nm.

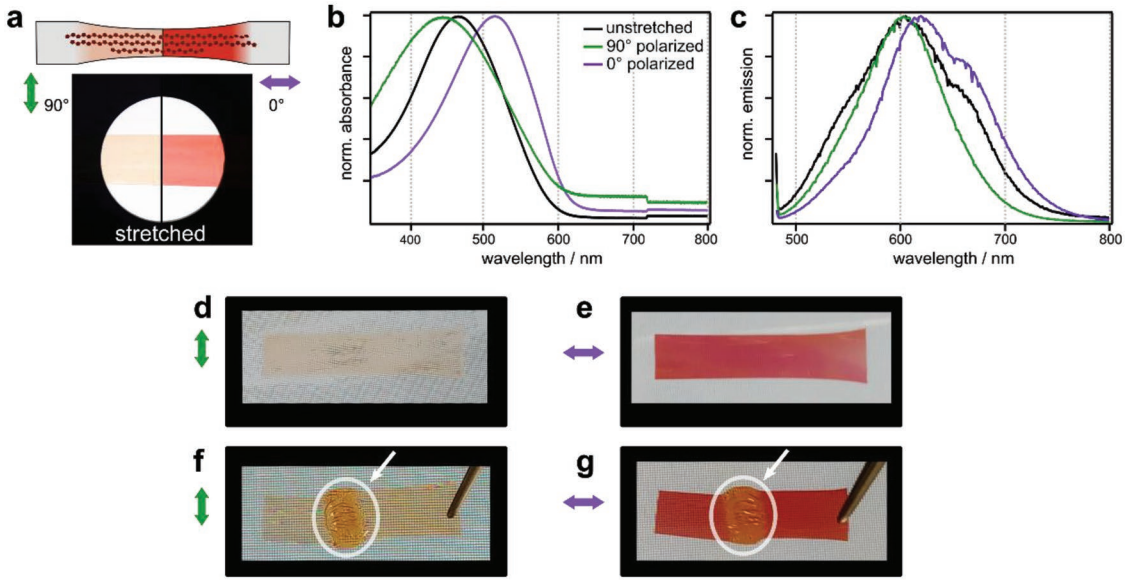

Figure 2. a) Scheme and polarized photographs of the stretched film. b) UV/vis absorption and c) emission spectra of the unstretched (black lines, no polarization) and stretched films (purple lines for 0° polarization and green lines for 90° polarization). d–g) Polarized photographs (d,f) for 90° and e,g) for 0° polarization) of the d,e) stretched films before and f,g) after locally heated (marked by circle and white arrows).

proton signal of the ex situ initiator's methyl group to calculate the degree of polymerization to be 39. The polymer has a number-averaged molecular weight M_n of 9022 g mol^{-1} and a polydispersity index (PDI) of 1.16 (gel permeation chromatography measurements in $CHCl_3$ at 40 °C, Figure S1b, Supporting Information). The narrow dispersity, the presence of the functional end-group, and the absence of any defects in monomer orientation confirm the well-defined molecular structure of P3TEOT, as we expected it from the chain-growth mechanism of the KCTP. Synthesis and analyses are presented in the Supporting Information. A detailed analysis study was published previously by our group.[41]

In aqueous solutions, P3TEOT possesses a lower critical solution temperature (LCST) at around 50 °C.[42] The LCST behavior arises from the amphiphilic character of this polymer, composed of the hydrophobic thiophene backbone and the hydrophilic TEO side-chains. At elevated temperatures, the TEO side-chains dehydrate and subsequently collapse,[43,44] which results in an aggregation-assisted planarization of the P3TEOT molecules.[45]

To explore the mechanochromic behavior, we prepared blends of P3TEOT with the highly polar, water-soluble polymer PVA. P3TEOT was incorporated into the PVA matrix by mixing the aqueous solutions of both polymers. First, we prepared blends with a content of P3TEOT of 1.35 wt% giving a bright orange-colored free-standing PVA film after the film-casting process (Figure 1b). These films (thickness = 0.5 mm) were cut into strips (10×50 mm^2), heated above the glass transition temperature of PVA ($T_g \approx 75$ °C)[46] and uniaxially stretched by 100% (Figure 1c). The accompanied color change from orange to red is readily apparent with the naked eye (Figure 1b). As presented in Figure 1d, UV-vis absorption measurements reveal a red-shift of λ_{max} from 460 nm up to 510 nm upon the stretching. The emission band is red-shifted as well (λ_{max} from 600 to 615 nm), however, to a smaller degree (Figure 1e).

Figure 2a shows the polarized photographs of the stretched film, where the strong linear dichroism of the stretched film is apparent by bare eyes. The film under polarized light parallel to the stretching direction (0°) displays a deep red color. For polarized light perpendicular to the stretching direction (90°), the film appears less intensely colored.

Not only the absorption peak position is changing upon the stretching but also its intensity. To quantify the increase of the intensity and the polarization, the films were investigated by a confocal scanning laser microscope (CLSM). The samples were excited with a 505 nm laser with circular polarization while the emitted light was filtered by a polarizing filter. This set-up enables to measure a defined volume, even though, the geometry of the film changes upon stretching. We found that the emission intensity increased with the polarization along the stretching direction by a factor of 3.3 with respect to the unstretched sample. For the polarization perpendicular to the stretching direction, the intensity decreased by a factor of 0.47.

To verify the reversibility of the mechanochromic changes, we locally heated the stretched film (Figure 2d,e) by pressing its middle part of the sample with a preheated tweezers for a few seconds (Figure 2f,g). For the polarization parallel to the stretching direction, the film immediately changes its color red to orange along with the randomization of the molecular orientation, as shown in Figure 2g. This color change was less clear but still visible for the polarization perpendicular to the stretching direction (Figure 2f).

To use P3TEOT blends for practical application such as for sensing of stress, it is important to determine a range of P3TEOT concentrations at which the change of the optical signal can be produced and detected. To this end, we fabricated a number of blend stripes with P3TEOT concentrations in the range of 1.3 to 10^{-6} wt%. We recorded their absorption and fluorescence in pristine state and at different stretching ratios. In the range from 1.3 to 0.1 wt%, the mechanochromism can be

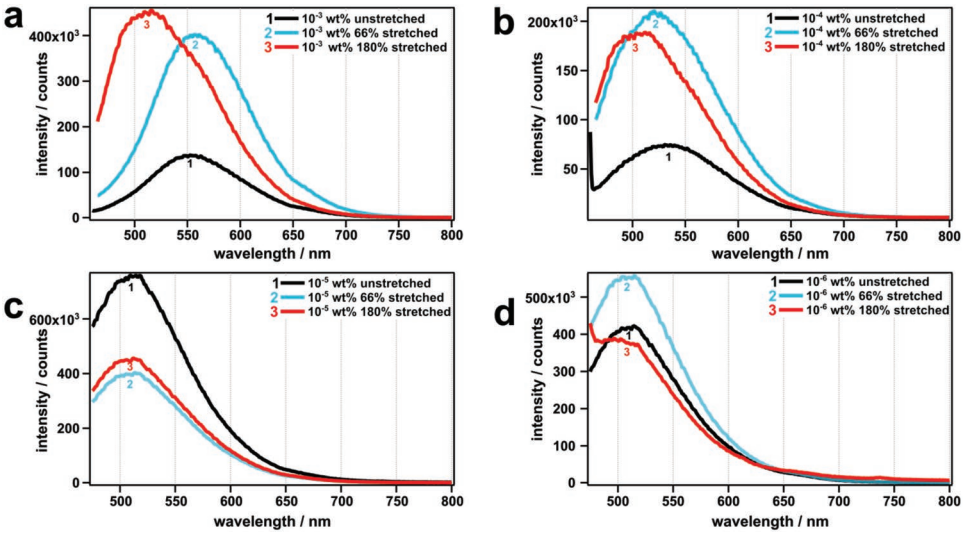

Figure 3. Fluorescence spectroscopy measurements of PVA films with a) 10^{-3}, b) 10^{-4}, c) 10^{-5}, and d) 10^{-6} wt% P3TEOT: unstretched (black lines, 1), stretched by 66% (blue lines, 2), and stretched by 180% (red lines, 3). Excitation wavelength is 450 nm.

visualized by the naked eye and was monitored quantitatively by UV-vis absorption spectroscopy. In this regime, the stretching results in a gradual red-shift of the absorption peak depending on the P3TEOT concentration. For the highest concentration of 1.35 wt%, we observed the largest shift from 467 to 509 nm. For lower concentrations (0.12 wt%), the shift decreases from 459 to 489 nm. At the concentration of 0.01 wt%, UV-vis spectroscopy detects still the optical absorption signal. However, the mechanochromism can no longer be observed properly (Figure S2, Supporting Information).

Since fluorescence spectroscopy is a more sensitive technique, it allows monitoring the P3TEOT fluorescence even at extremely low concentrations down to 10^{-6} wt% (**Figure 3**). The sample containing 10^{-3} wt% of P3TEOT shows an emission maximum of 553 nm in the unstretched state (Figure 3a). Upon stretching the film by 66%, its fluorescence intensity increases by a factor of 2.5. The position of the maximum emission and the peak shape remain almost unchanged. Further stretching of the same film, in total by 180%, leads to an additional but minor intensity increase and a significant change of the peak shape: the emission with λ_{max} = 553 nm decreases while a new peak with λ_{max} = 511 nm emerges. As a result of the stretching, the thickness of the films reduces (we assume that the volume stays constant). For elongation of 180%, the thickness is decreased by 36.5–38.5%. Taking this thickness reduction into account, we determined an increase of the fluorescence intensity by a factor of 4.4 during the total film stretching. This enhancement is in agreement with the intensity enhancement of 3.3, which we determined previously by CLSM.

In the opposite extreme, at extreme dilutions, e.g., below 10^{-5} wt%, aggregates split to individual molecules (**Figure 4**c).

Qualitatively similar behavior is observed for the film with 10^{-4} wt% of P3TEOT (Figure 3b). Here, the unstretched film shows a maximum of 533 nm, which blue-shifts to 521 nm upon the stretching by 66%. The fluorescence peak shifts further to 503 nm by stretching the film further by 180%. This blue-shifted peak appears only as a shoulder to the main signal, peaking at 518 nm (Figure 3b). Similarly to the 10^{-3} wt% sample, the 66% stretching is accompanied by a 3.6 times increase in fluorescence intensity and the intensity remains approximately constant upon further stretching up to 180%. When P3TEOT is further diluted in the PVA matrix down to 10^{-5} wt% (Figure 3c) and 10^{-6} wt% (Figure 3d), the emission maximum stays at the blue-shifted position around 505 nm and the fluorescence intensity remains almost constant upon the stretching.

We suggest that the fully planar conformation with an *all-trans* arrangement is unfavored for single P3TEOT molecules embedded into polar PVA environment because in this case, the side TEO groups can efficiently protect only molecular "edges" leaving unprotected the molecular "planes," as shown in Figure 4d. Instead, we anticipate that in this case, the molecular chains are strongly twisted with TEO chains evenly extend from the backbone. This twisted conformation decreases unfavored interactions of the hydrophobic backbone with the polar environment and is responsible for the blue-shifted fluorescence. The shear-induced stretching and planarization of molecules is strongly unfavored process because in the planar conformation, both molecular planes remain unprotected from polar environment, as discussed above (Figure 2d). As a consequence, no mechanochromism is observed at extreme dilutions.

The semidiluted regime (10^{-2} to 10^{-4} wt%, Figure 4b) shares features of both concentration extremes. In this case, we anticipate the formation of small aggregates, which adopt an intermediate conformation (Figure 4b). Thus, the dilution gradually splits larger aggregates of planar molecules onto smaller aggregates of more twisted molecules or even onto strongly twisted single chains, which accounts to the fluorescence blue-shift. As discussed above, efficient shear-induced planarization requires for P3TEOT molecules to be well-stacked. However, because the fraction of stacked molecules in small aggregates is small, the planarization and association with this red-shift of the fluorescence are not observed in the semidiluted concentration

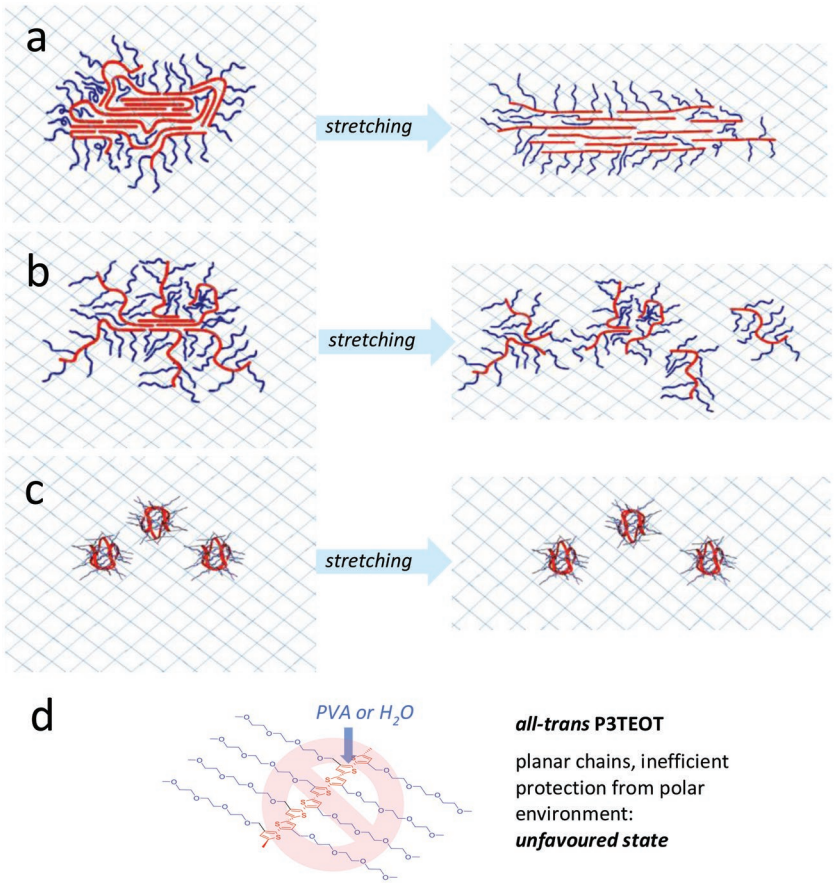

Figure 4. Schematic representation of stretching-induced transformations of P3TEOT/PVA blends in different concentration regimes. a) High concentration regime (0.1–1 wt%): polymer chains in crew-cut aggregates are further planarized and aligned upon stretching. b) Intermediate concentration regime (10^{-4} to 10^{-2} wt%): the small micelles/aggregates are separated into individual unimers upon stretching. c) Diluted concentration regime (10^{-6} to 10^{-5} wt%): separated unimers, with no response upon stretching. d) Fully planar conformation of P3TEOT represents an unfavored state in polar environment if molecules are not aggregated because their hydrophobic molecular planes (shown by the blue arrow) are exposed to polar media.

regime. Instead, the stretching deforms the micelles, which increases the interface between the polar PVA matrix and the upolar part of P3TEOT aggregates. This, in turn, derives an additional molecular twist and, consequently, the blue-shift of the fluorescence. Another distinct feature of the stretching process is increase of the fluorescence intensity, as a result of disaggregation and decreased self-quenching phenomenon. In general, the stretching process here is reminiscent the dilution process as both processes cause additional twisting of the P3TEOT chains.

In conclusions, we have established a novel mechanism for well-pronounced reversible mechanochromism, which is based on conformation transitions of a chromophore rather than caused by different aggregation states of the chromophore. It was particularly found that blends of the water-soluble π-CP P3TEOT embedded into the matrix of thermoplastic polymer PVA, upon stretching, undergo either a strong red-shift of the light absorption (λ_{max} from 460 to 510 nm) at high P3TEOT concentrations or a strong blue shift of the emission ($\lambda_{max,\,em}$ from 600 to 503 nm), at low concentrations. This counterintuitive phenomenon can be explained in terms of the concentration dependency of the P3TEOT's aggregation state, which in turn results in different molecular conformations and optical properties. The mechanochromic transitions are fully reversible and initial conformational state and isotropic structure can be recovered upon a brief heating above glass transition point of PVA or in the presence of moisture. The unique ability of P3TEOT blends to change color upon the stretching is due to an "intermediate," moderately planar conformation of P3TEOT in the solid state[47] and because of its low glass transition temperature. A combination of these two factors is responsible for mobility of P3TEOT chain and their transition to more planar states upon the stretching at high concentrations of P3TEOT or to twisted states, at low concentrations of P3TEOT. An advantage of the P3TEOT/PVA-based mechanochromic system is that the optical response can be monitored at unprecedentedly low concentration of the chromophore down to 10 ppm.

Experimental Section

Preparation of Samples: The aqueous stock solutions of PVA (Aldrich) and P3TEOT (M_n = 9500 g mol^{-1}, PDI = 1.16 was synthesized by the ex situ initiated KTCP[40,41]) were mixed in water to give the desired concentrations, which was 6 wt% for PVA and the following for P3TEOT: 1.3, 0.13, 1.3 × 10^{-1}, 1.3 × 10^{-2}, 1.3 × 10^{-3}, and 1.3 × 10^{-4} wt%. The blended solution was degassed in a desiccator by applying reduced pressure and subsequent drying for 1 week. The blended PVA films were stretched by heating the P3TEOT-PVA blend above the T_G (≈75 °C)[46] of PVA with a heatgun and stretched manually. The diluted thin films of the P3TEOT/PVA blend were prepared on a silicon substrate by spin-coating. The aqueous solutions of both polymers were pre-mixed to give the final concentrations of 0.91 µg mL^{-1} for P3TEOT and 5 wt% for PVA. The film thickness of 8 nm was determined by the razor-blade cut method with atomic force microscopy.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

conjugated polymers, mechanical strain, mechanochromism, polymer blends, polythiophenes

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